

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 May 2002 (02.05.2002)

PCT

(10) International Publication Number
WO 02/34739 A1

(51) International Patent Classification⁷: C07D 321/10,
C09K 19/34, 19/58 // C07M 7:00

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(21) International Application Number: PCT/EP01/11075

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(22) International Filing Date:

25 September 2001 (25.09.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

00122844.4	20 October 2000 (20.10.2000)	EP
00123385.7	31 October 2000 (31.10.2000)	EP
01104842.8	28 February 2001 (28.02.2001)	EP

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CHIRAL BINAPHTHOL DERIVATIVES

(57) Abstract: The invention relates to chiral binaphthol derivatives of formula (I) wherein Y¹, Y², W¹ and W² have the meaning given in claim 1, to liquid crystalline mixtures comprising at least one chiral binaphthol derivative of formula (I), to chiral-linear or crosslinked liquid crystalline polymers obtainable by polymerizing a polymerizable mixture comprising at least one chiral binaphthol derivative of formula (I), to the use of chiral binaphthol derivatives of formula (I) and mixtures and polymers obtained thereof in liquid crystal displays, active and passive optical elements, adhesives, synthetic resins with anisotropic mechanical properties, cosmetic and pharmaceutical compositions, diagnostics, liquid crystal pigments, for decorative and security applications, nonlinear optics, optical information storage or as chiral dopants, and to a liquid crystal display comprising a mixture comprising at least one chiral binaphthol derivative of formula (I).

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Chiral Binaphthol Derivatives

The invention relates to chiral binaphthol derivatives, to liquid crystalline mixtures containing the chiral binaphthol derivatives, to polymers obtained from the chiral binaphthol derivatives and liquid crystalline mixtures, and to the use of the chiral binaphthol derivatives, liquid crystalline mixtures and polymers obtained thereof in liquid crystal displays, active and passive optical elements like polarizers, compensators, alignment layers, colour filters or holographic elements, in adhesives, synthetic resins with anisotropic mechanical properties, cosmetic and pharmaceutical compositions, diagnostics, liquid crystal pigments, for decorative and security applications, in nonlinear optics, optical information storage or as chiral dopants.

Chiral compounds can be used as dopants to induce or enhance a helical twist in a liquid crystalline mixture that is used for example in liquid crystal displays. The pitch p of the molecular helix in the first approximation, which is sufficient for most practical applications, is inversely proportional to the concentration c of the chiral dopant in the liquid crystal host mixture according to equation (1) :

$$p = \frac{1}{\text{HTP}} \cdot \frac{1}{c} \quad (1)$$

The proportionality factor is the helical twisting power (HTP) of the chiral dopant.

For many applications it is desirable to have LC mixtures with a twisted phase. Among these are e.g. phase-change displays, guest-host displays, passive and active matrix TN and STN displays like AMD-TN, ferroelectric displays and cholesteric displays like SSCT (surface stabilized cholesteric texture) or PSCT (polymer stabilized cholesteric texture) displays, including displays with temperature compensated characteristics, e.g. by appropriate selection of the cholesteric compounds according to the invention either alone or in combination

with further chiral dopants. For these applications it is advantageous to have available a chiral dopant with a high HTP in order to reduce the amount of dopant needed to induce the desired pitch.

5 For some applications it is desired to have LC mixtures that exhibit a strong helical twist and thereby a short pitch length. For example in liquid crystalline mixtures that are used in selectively reflecting cholesteric displays like SSCT or PSCT, the pitch has to be selected such that the maximum of the wavelength reflected by the cholesteric helix is in the
10 range of visible light. Another possible application are polymer films with a chiral liquid crystalline phase for optical elements, such as cholesteric broadband polarizers or chiral liquid crystalline retardation films.

15 As can be seen from equation (1), a short pitch can be achieved by using high amounts of dopant or by using a dopant with a high HTP.

Chiral compounds are disclosed for example in WO 95/16007, WO 98/00428 and GB 2 328 207 A.

20 However, the chiral dopants of prior art often exhibit low values of the HTP, so that high amounts of dopant are needed. This is a disadvantage because chiral dopants can be used only as pure enantiomers and are therefore expensive and difficult to synthesize.

25 Furthermore, when using chiral dopants of prior art in high amounts, they often negatively affect the properties of the liquid crystalline host mixture, such as e.g. the clearing point, the dielectric anisotropy $\Delta\epsilon$, the viscosity, the driving voltage or the switching times.

30 Another disadvantage of prior art chiral compounds is that they often show low solubility in the liquid crystal host mixture, which leads to undesired crystallization at low temperatures. To overcome this disadvantage, typically two or more different chiral dopants have to be added to the host mixture. This implies higher costs and also
35 requires additional effort for temperature compensation of the

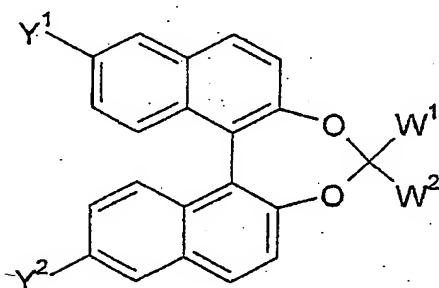
mixture, as the different dopants have to be selected such that their temperature coefficients of the twist compensate each other.

Consequently, there is a considerable demand for chiral compounds with a high HTP which are easy to synthesize, can be used in low amounts, show improved temperature stability of the cholesteric pitch e.g. for utilizing a constant reflection wavelength, do not affect the properties of the liquid crystalline host mixture and show good solubility in the host mixture.

The invention has the aim of providing chiral compounds having these properties, but which do not have the disadvantages of the chiral dopants of the state of the art as discussed above.

Another aim of the invention is to extend the pool of chiral compounds that can be used as dopants available to the expert.

It has been found that these aims can be achieved by providing chiral binaphthol derivatives of formula I.



wherein

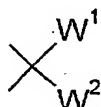
Y¹ and Y² are independently of each other H, F, Cl, Br, I, CN, SCN, SF₅, or a chiral or achiral alkyl group with up to 30 C atoms which may be unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-,

-N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-,
-CO-S-, -CH=CH- or -C≡C- in such a manner that
oxygen atoms are not linked directly to one another, or a
polymerizable group,

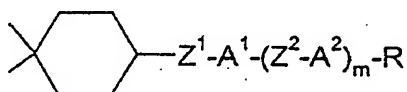
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one of W¹ and W² is -Z¹-A¹-(Z²-A²)_m-R and the other is H, R² or A³, or
both of W¹ and W² are -Z¹-A¹-(Z²-A²)_m-R, with W¹ and
W² not being at the same time H, or

10



is



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Z¹ and Z² are independently of each other -O-, -S-, -CO-,
-COO-, -OCO-, -O-COO-, -CO-N(R¹)-, -N(R¹)-CO-,
-OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-,
-CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-,
-CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CH-, -CF=CH-,
-CH=CF-, -CF=CF-, -C≡C-, -CH=CH-COO-, -OCO-
CH=CH- or a single bond,

20

R¹ is H or alkyl with 1 to 4 C atoms,

25

A¹, A² and A³ are independently from one another 1,4-phenylene in
which, in addition, one or more CH groups may be
replaced by N, 1,4-cyclohexylene in which, in addition,
one or two non-adjacent CH₂ groups may be replaced by
O and/or S, 1,3-dioxolane-4,5-diyl, 1,4-cyclohexenylenes,
1,4-bicyclo-(2,2,2)-octylene, piperidine-1,4-diyl,
naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl,
1,2,3,4-tetrahydronaphthalene-2,6-diyl or indane-2,5-
diyl, it being possible for all these groups to be
unsubstituted, mono- or polysubstituted with halogen,
cyano or nitro groups or alkyl, alkoxy, alkylcarbonyl or
alkoxycarbonyl groups with 1 to 7 C atoms, wherein one

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or more H atoms may be substituted by F or Cl, and A¹ may also be a single bond,

m is in each case independently 0, 1, 2 or 3, and

R and R² have independently of each other one of the meanings given for Y¹.

Another object of the invention is a liquid crystalline mixture containing at least one compound of formula I:

Another object of the present invention is a polymerizable liquid crystalline mixture comprising at least one compound of formula I and at least one polymerizable mesogenic compound having at least one polymerizable functional group.

Another object of the invention is a chiral linear or crosslinked liquid crystalline polymer obtainable by polymerizing a polymerizable liquid crystalline mixture comprising one or more compounds of formula I.

A further object of the invention is the use of a chiral compound, mixture or polymer as described above in liquid crystal displays, such as STN, TN, AMD-TN, temperature compensation, ferroelectric, guest-host, phase change or surface stabilized or polymer stabilized cholesteric texture (SSCT, PSCT) or active broadband polymer stabilized liquid crystal displays, in active and passive optical elements like polarizers, compensators, alignment layers, colour filters or holographic elements, in adhesives, synthetic resins with anisotropic mechanical properties, cosmetic and pharmaceutical compositions, diagnostics, liquid crystal pigments, for decorative and security applications, in nonlinear optics, optical information storage or as chiral dopants.

Yet another object of the invention is a liquid crystal display comprising a liquid crystalline mixture or a polymerizable liquid crystalline mixture comprising at least one chiral compound of formula I.

The inventive chiral compounds bear several advantages

- they exhibit a high HTP,
- 5 • they exhibit a good solubility in liquid crystalline mixtures,
- they exhibit broad liquid crystalline phases,
- when inventive compounds are used as chiral dopant in a liquid crystalline mixture, due to their high solubility higher amounts of dopant can be used to produce a high twist (= a low pitch),
- 10 • in case high amounts of dopants are needed, due to the broad liquid crystalline phases of the inventive dopants the liquid crystal phase of the host mixture is less negatively influenced,
- due to their high HTP, lower amounts of inventive dopants are needed to achieve a high pitch, and thereby the liquid crystalline properties of the mixture are less negatively affected,
- 15 • liquid crystalline mixtures comprising one or more inventive dopants show a considerably improved low temperature stability,
- nematic liquid crystalline mixtures comprising one or more inventive dopants show a reduced temperature dependence of the threshold voltage when used in electrically switchable displays,
- 20 • enantiomerically pure inventive chiral compounds are easy to prepare from cheap, readily available starting materials,
- 25 • the availability of both helices is a considerable advantage, e.g. for the use in security applications, as it enables the production of chiral films or coatings reflecting circularly polarized light of a single handedness.
- 30

The inventive chiral compounds are mesogenic or even liquid crystalline, i.e. they can induce or enhance mesophase behaviour for example in admixture with other compounds, or even exhibit one or more mesophases themselves. It is also possible that the inventive compounds show mesophase behaviour only in mixtures with other compounds, or, in case of polymerizable compounds, when being

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(co)polymerized. Mesogenic inventive chiral compounds are especially preferred.

5

Very preferred are compounds of formula I wherein Y^1 and Y^2 are H.

Further preferred are compounds of formula I wherein at least one of Z^1 and Z^2 is $-\text{CF}_2\text{O}-$, $-\text{OCF}_2-$ or $-\text{CF}_2\text{CF}_2-$. These compounds have a particular high solubility in liquid crystalline mixtures.

10

Also preferred are compounds of formula I wherein Z^1 is a single bond.

Further preferred are compounds of formula I wherein at least one of Z^1 and Z^2 is $-\text{CF}_2\text{O}-$, $-\text{OCF}_2-$, $-\text{CF}_2\text{CF}_2-$ or $-\text{CF}=\text{CF}-$ and the other is $-\text{COO}-$, $-\text{OCO}-$, $-\text{CH}_2\text{-CH}_2-$ or a single bond.

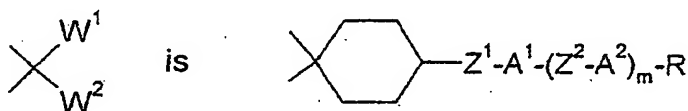
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Another preferred embodiment relates to compounds of formula I wherein at least one of Z^1 and Z^2 denotes $-\text{C}\equiv\text{C}-$. These compounds are especially suitable for uses where highly birefringent materials are needed.

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Further preferred are compounds of formula I wherein

25



and wherein m is 0 or 1, especially preferably 0, furthermore those wherein m is 0 and A^1 is a single bond.

30

Further preferred are compounds of formula I, wherein W^1 is H, R^2 or A^3 and W^2 is $-Z^1-A^1-(Z^2-A^2)_m-R$ with m being 1 or 2, and compounds wherein W^1 and W^2 are $-Z^1-A^1-(Z^2-A^2)_m-R$ with m being 1 or 2.

35

Further preferred are compounds wherein W^1 is H, R^2 or A^3 and W^2 is a polymerizable group.

5 R^2 in these compounds is preferably F or straight chain alkyl with 1 to 12 C atoms wherein one or more H atoms may be replaced with F or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another. Very preferably R^2 is F or alkyl or alkoxy with 1 to 12 C atoms.

10 A^3 in these compounds is preferably 1,4-phenylene or 1,4-cyclohexylene that is optionally substituted in 1 to 5, very preferably 1, 2 or 3 positions with F, Cl, CN, NO₂, or alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl groups with 1 to 4 C atoms wherein one or more H atoms may be substituted by F or Cl.

15 Further preferred are compounds of formula I wherein the mesogenic group $-Z^1-A^1-(Z^2-A^2)_m$ incorporates one, two or three five- or six-membered rings.

20 Particularly preferred are compounds of formula I wherein A^1 and A^2 are selected of 1,4-phenylene and trans-1,4-cyclohexylene, these rings being unsubstituted or substituted in 1 to 4 positions with F, Cl, CN or alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl with 1 to 4 C-atoms. From these preferred compounds, especially preferred are
25 those comprising a bicyclohexyl or cyclohexylphenyl group.

A smaller group of preferred mesogenic groups $-Z^1-A^1-(Z^2-A^2)_m$ is listed below. For reasons of simplicity, Phe in these groups is 1,4-phenylene which may also substituted by at least one group L, with L
30 being F, Cl, CN or an optionally fluorinated alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl group having 1 to 4 C atoms, Cyc is 1,4-cyclohexylene and Z has in each case independently one of the meanings of Z^1 in formula I. The list of preferred mesogenic groups is comprising the following formulae as well as their mirror images

35

-Phe-

II-1

	-Cyc-	II-2
	-Phe-Z-Phe-	II-3
	-Phe-Z-Cyc-	II-4
	-Cyc-Z-Cyc-	II-5
5	-Phe-Z-Phe-Z-Phe-	II-6
	-Phe-Z-Phe-Z-Cyc-	II-7
	-Phe-Z-Cyc-Z-Phe-	II-8
	-Cyc-Z-Phe-Z-Cyc-	II-9
	-Cyc-Z-Cyc-Z-Phe-	II-10
10	-Cyc-Z-Cyc-Z-Cyc-	II-11

Particularly preferred are the subformulae II-3, II-4, II-5, II-6, II-7 and II-10, in particular II-4 and II-5.

15 Further preferred are subformula II-5, wherein Z is $-\text{CF}_2\text{CF}_2-$ and subformula II-3 and II-4, wherein Z is $-\text{OCF}_2-$.

Further preferred are subformulae II-10 and II-11, wherein one or both of Z between two cyclohexylene rings are $-\text{CF}_2\text{CF}_2-$, and subformulae
20 II-6, II-7, II-8, II-9, and II-10, wherein one or both of Z between two phenylene rings or between a phenylene and a cyclohexylene ring are $-\text{OCF}_2-$ or $-\text{CF}_2\text{O}-$, with the O atom being adjacent to the phenylene ring.

25 The other groups Z are preferably $-\text{COO}-$, $-\text{OCO}-$, $-\text{CH}_2\text{CH}_2-$ or a single bond.

Further preferred are compounds wherein the mesogenic group comprises at least one group Phe that is substituted with one or two groups L, preferably in 3- and/or 5-position, further preferably in 2-
30 and/or 3-position, and L is F, Cl, CH_3 , OCH_3 , CF_3 , CHF_2 , CH_2F , OCF_3 , OCHF_2 , OCH_2F or CN.

L is preferably F, Cl, CN, NO_2 , CH_3 , C_2H_5 , OCH_3 , OC_2H_5 , COCH_3 , COC_2H_5 , CF_3 , CHF_2 , CH_2F , OCF_3 , OCHF_2 , OCH_2F , OC_2F_5 , in particular
35 F, Cl, CN, CH_3 , CHF_2 , C_2H_5 , OCH_3 , OCHF_2 , CF_3 and OCF_3 , most preferably F, CH_3 , CF_3 , OCH_3 , OCHF_2 and OCF_3 .

If Y^1 , Y^2 or R in formula I is an alkyl or alkoxy radical, i.e. where the terminal CH_2 group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

Oxaalkyl, i.e. where one CH_2 group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

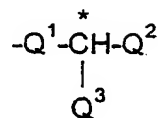
Halogen is preferably F or Cl.

Y^1 , Y^2 or R in formula I can be a polar or an unpolar group. In case of a polar group, it is selected from CN, SF_5 , halogen, OCH_3 , SCN, COR^5 , $COOR^5$ or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms. R^5 is optionally fluorinated alkyl with 1 to 4, preferably 1 to 3 C atoms. Especially preferred polar groups are selected of F, Cl, CN, OCH_3 , $COCH_3$, COC_2H_5 , $COOCH_3$, $COOC_2H_5$, CF_3 , CHF_2 , CH_2F , OCF_3 , $OCHF_2$, OCH_2F , C_2F_5 and OC_2F_5 , in particular F, Cl, CN, CF_3 , $OCHF_2$ and OCF_3 .

In case of an unpolar group, Y^1 , Y^2 or R is preferably alkyl with up to 15 C atoms or alkoxy with 2 to 15 C atoms.

Y^1 , Y^2 or R in formula I can be an achiral or a chiral group. In case of a chiral group it is preferably selected according to formula III:

35



III

5 wherein

Q^1 is an alkylene or alkylene-oxy group with 1 to 9 C atoms or a single bond,

10 Q^2 is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by F, Cl, Br or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by
 15 $\text{---C}\equiv\text{C---}$, ---O--- , ---S--- , ---NH--- , $\text{---N(CH}_3\text{)---}$, ---CO--- , ---COO--- , ---OCO--- , ---OCO-O--- , ---S-CO--- or ---CO-S--- in such a manner that oxygen atoms are not linked directly to one another,

Q^3 is F, Cl, Br, CN or an alkyl or alkoxy group as defined for Q^2 but being different from Q^2 .

20

In case Q^1 in formula III is an alkylene-oxy group, the O atom is preferably adjacent to the chiral C atom.

25 Preferred chiral groups of formula III are 2-alkyl, 2-alkoxy, 2-methylalkyl, 2-methylalkoxy, 2-fluoroalkyl, 2-fluoroalkoxy, 2-(2-ethin)-alkyl, 2-(2-ethin)-alkoxy, 1,1,1-trifluoro-2-alkyl and 1,1,1-trifluoro-2-alkoxy.

Particularly preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-hexyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-

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5 methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, 1,1,1-trifluoro-2-octyloxy, 1,1,1-trifluoro-2-octyl, 2-fluoromethyloctyloxy for example. Very preferred are 2-hexyl, 2-octyl, 2-octyloxy, 1,1,1-trifluoro-2-hexyl, 1,1,1-trifluoro-2-octyl and 1,1,1-trifluoro-2-octyloxy.

10 In addition, compounds of formula I containing an achiral branched group Y^1 , Y^2 or R may occasionally be of importance, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropoxy and 3-methylbutoxy.

In another preferred embodiment Y^1 , Y^2 or R in formula I denote a polymerizable group P-Sp-X, with

20 P being $CH_2=CH-COO-$, $WCH=CH-O-$, $WHC \begin{array}{c} \diagup O \diagdown \\ \text{---} \end{array} CH-$ or $CH_2=CH-Phenyl-(O)_k-$, W being H, CH_3 or Cl and k being 0 or 1,

Sp being a spacer group having 1 to 25 C atoms or a single bond,

25 X being $-O-$, $-S-$, $-OCH_2-$, $-CH_2O-$, $-CO-$, $-COO-$, $-OCO-$, $-OCO-O-$, $-CO-N(R^1)-$, $-N(R^1)-CO-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CH=CH-COO-$, $-OOC-CH=CH-$ or a single bond, and

R^1 being H or alkyl with 1 to 4 C atoms.

30 P is preferably a vinyl group, an acrylate group, a methacrylate group, a propenyl ether group or an epoxy group, especially preferably an acrylate or a methacrylate group.

35 In another preferred embodiment P is a branched group comprising two or more reactive moieties, like for example a group selected from

-OCO-CR⁰(CH₂-OCO-CW=CH₂)₂ and -OCO-C(CH₂-OCO-CW=CH₂)₃, with W being H, Cl or CH₃ and R being H or alkyl with 1 to 4 C atoms, preferably H or methyl.

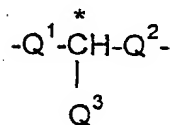
5 As for the spacer group Sp all groups can be used that are known for this purpose to the skilled in the art. The spacer group Sp is preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH₂ groups may be replaced by -O-, -S-, -NH-,
10 -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CH(halogen)-, -CH(CN)-, -CH=CH- or -C≡C-.

Typical spacer groups are for example -(CH₂)_p-, -(CH₂CH₂O)_r-CH₂CH₂-,
15 -CH₂CH₂-S-CH₂CH₂- or -CH₂CH₂-NH-CH₂CH₂-, with p being an integer from 2 to 12 and r being an integer from 1 to 3.

Preferred spacer groups are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-
20 iminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene for example.

Especially preferred are inventive chiral compounds of formula I
25 wherein Sp-X is denoting alkyl or alkoxy with 2 to 6 C atoms. Straight-chain alkyl or alkoxy groups are especially preferred.

In another preferred embodiment of the invention the chiral compounds comprise at least one spacer group Sp that is a chiral
30 group of formula IV:



IV

35 wherein

- Q¹ is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,
- 5 Q² is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q¹, and
- Q³ is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q².

- 10 In case Q¹ in formula IV is an alkylene-oxy group, the O atom is preferably adjacent to the chiral C atom.

- Another preferred embodiment relates to compounds of formula I comprising a photoisomerizable group, for example a group with a
15 C=C, C=N or N=N double bond. These compounds change their shape, for example by E-Z- or cis-trans isomerization, upon photoirradiation e.g. with UV light.

- Particularly preferred are photoisomerizable compounds of formula I
20 wherein one or both of W¹ and W² denote -Z¹-A¹-(Z²-A²)_m-R and Z¹ or Z² is a photoisomerizable group, in particular -CH=CH-COO- or -OCO-CH=CH-. Very particularly preferred are photoisomerizable compounds of formula I wherein W¹ is -Z¹-A¹-(Z²-A²)_m-R and Z¹ is -OCO-CH=CH-.

- 25 Photolysis of photoisomerizable compounds of formula I with e.g. UV light of 360 nm has the effect of isomerising the double bond of the photoisomerizable group from E to Z, thus completely changing the shape of the molecule and hence the physical molecular properties
30 like the twisting power.

- The chiral compounds of formula I can be mixed with other mesogenic compounds to give a chiral liquid crystalline mixture. If such a liquid crystalline mixture, for example a cholesteric mixture is coated as a
35 thin layer and aligned on a surface and then photolysed with e.g. UV light of 360 nm, the light changes the shape of the isomerizable

dopant – this in turn reduces the HTP, and this has an overall effect of increasing the pitch and thus the reflection wavelength of the mixture.

5 If irradiation is carried out through a photomask towards the layer of the liquid crystalline mixture doped with the chiral photoisomerizable compound, a pattern in the shape of the photomask is obtained, where different regions of the layer show different reflection wavelength. If the photoisomerizable compound and/or the other compounds of the mixture are polymerizable compounds, this pattern can be fixed by in-
10 situ polymerization of the mixture.

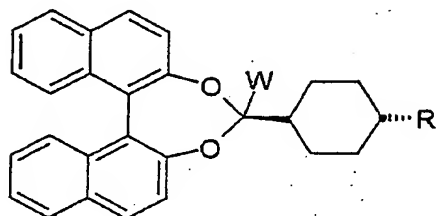
As the change of the HTP of the chiral photoisomerizable compound of formula I depends on the intensity of photoradiation, the change of the twist in the mixture can also be controlled by local variation of the
15 radiation intensity, e.g. by the use of grey filters alternatively or in addition to a photomask.

It is also possible to achieve a change of the twist in a direction vertical to the plane of the layer by adding a dye to the mixture that
20 has an absorption maximum at the wavelength where the isomerizable compound shows photoisomerization, for example a UV dye. The dye will create a gradient in intensity of photoradiation throughout the thickness of the layer, so that the isomerization and thus the change of twist is faster at the top of the layer than at the
25 bottom. In this way a pitch gradient is created, leading to a broadening of the reflected wavelength band. This method is especially useful for the preparation of broadband reflective polarizers.

30 The chiral photoisomerizable compounds of formula I are thus suitable e.g. for forming patterned films, which can be used for example as reflective polarizers or colour filters for LC displays, for decorative or security applications such as security markings for ID cards, labels or documents of value, in nonlinear optics, for optical
35 recording or information storage.

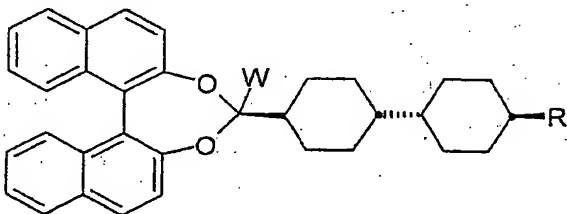
Particularly preferred are the following compounds of formula I

5



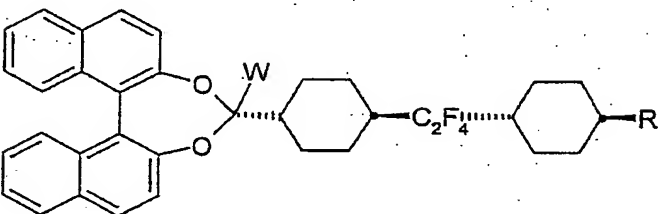
1a

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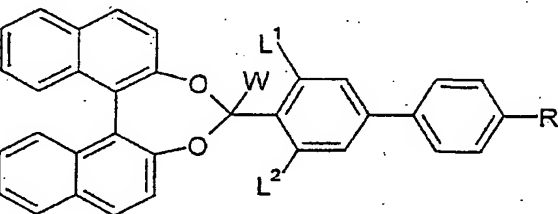
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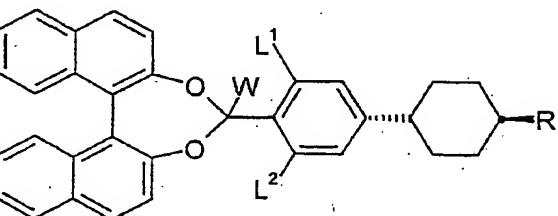
1c

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1d

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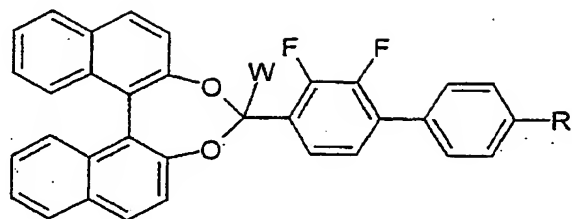


1e

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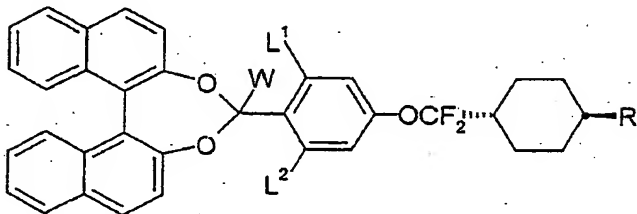
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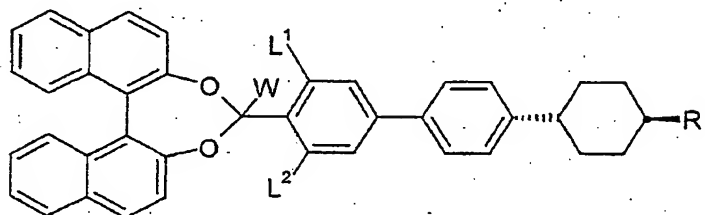
If

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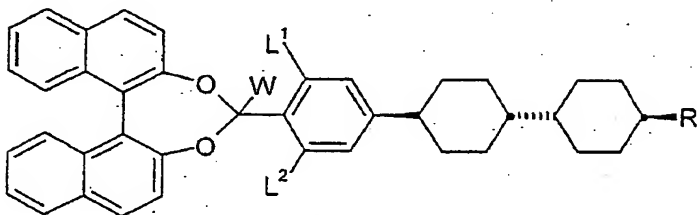
Ig

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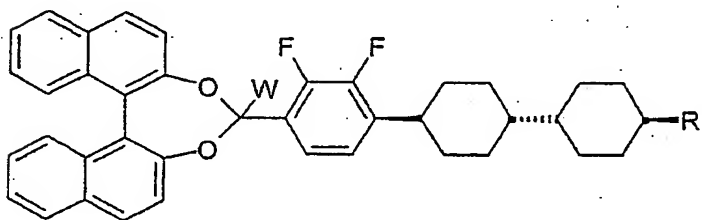
Ih

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Ii

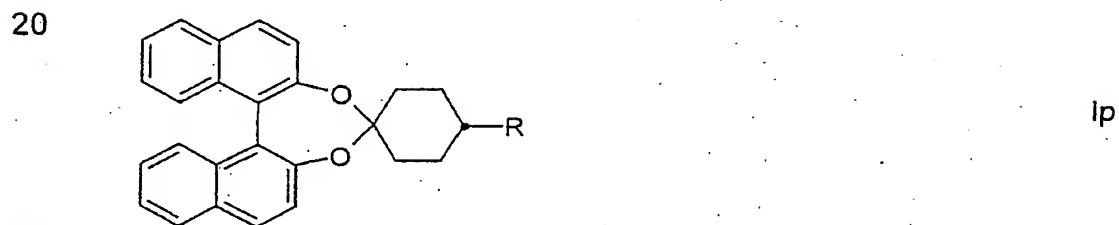
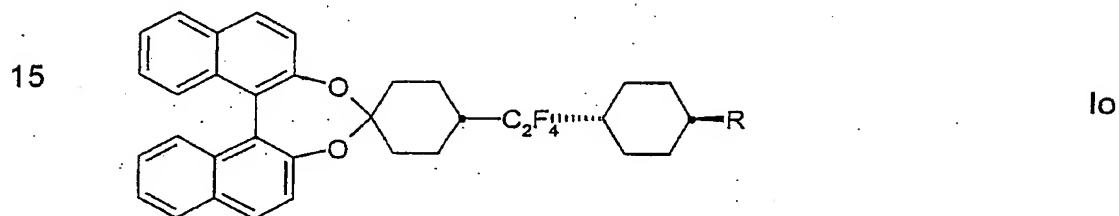
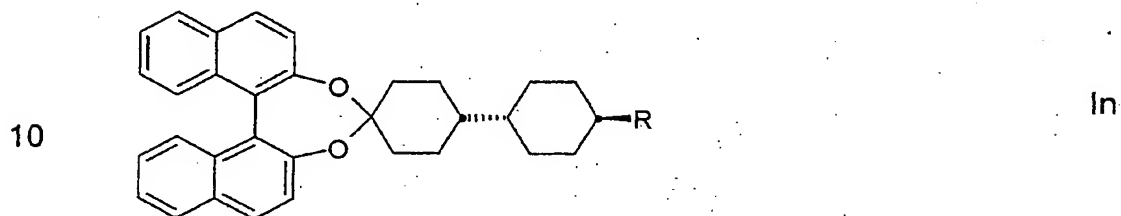
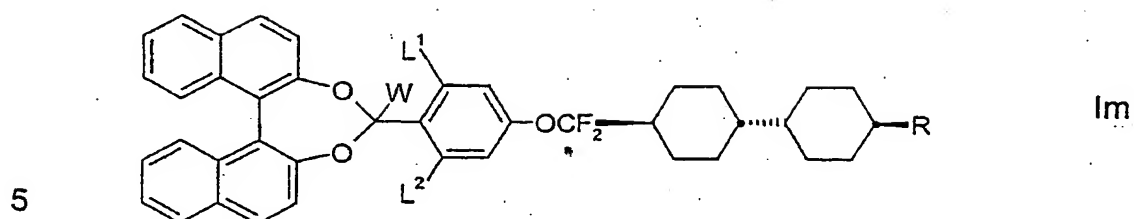
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Ik

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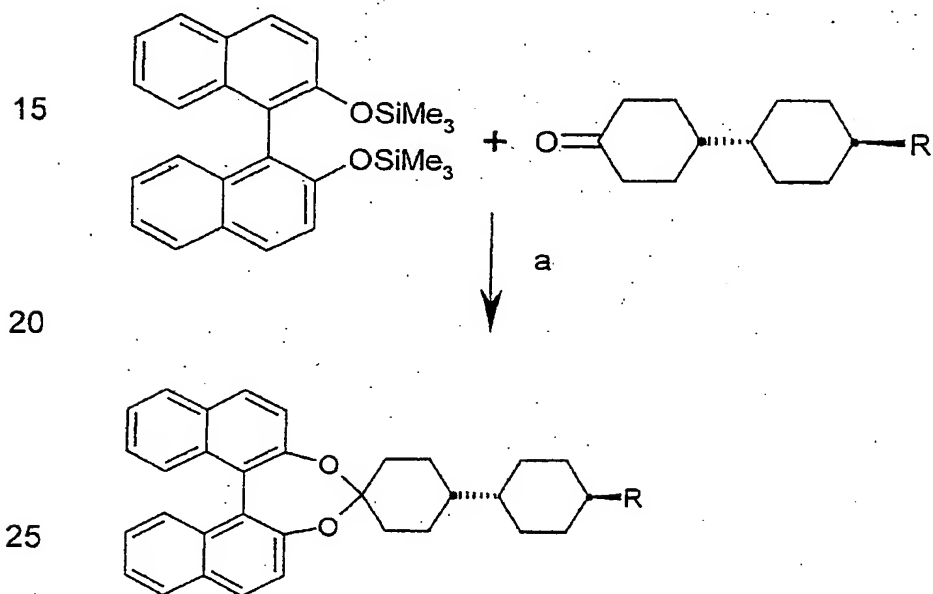
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wherein R has one of the above meanings, L^1 and L^2 are H or F and W is H, F, alkyl or alkoxy with 1 to 12 C atoms, cyclohexyl or phenyl that can be substituted in 1 to 4 positions with L as defined above.

Particularly preferred are compounds of formula Ia to Ip wherein W is H or F, very preferably H.

The inventive chiral compounds can be synthesized according to or in analogy to known methods, for example as described in M. Zhang and G.B. Schuster, J. Am. Chem. Soc. 1994, 116, 4852-4857. In particular, they can be prepared according to or in analogy to the following reaction schemes. Further methods for preparing the inventive compounds can be taken from the examples.

Scheme 1

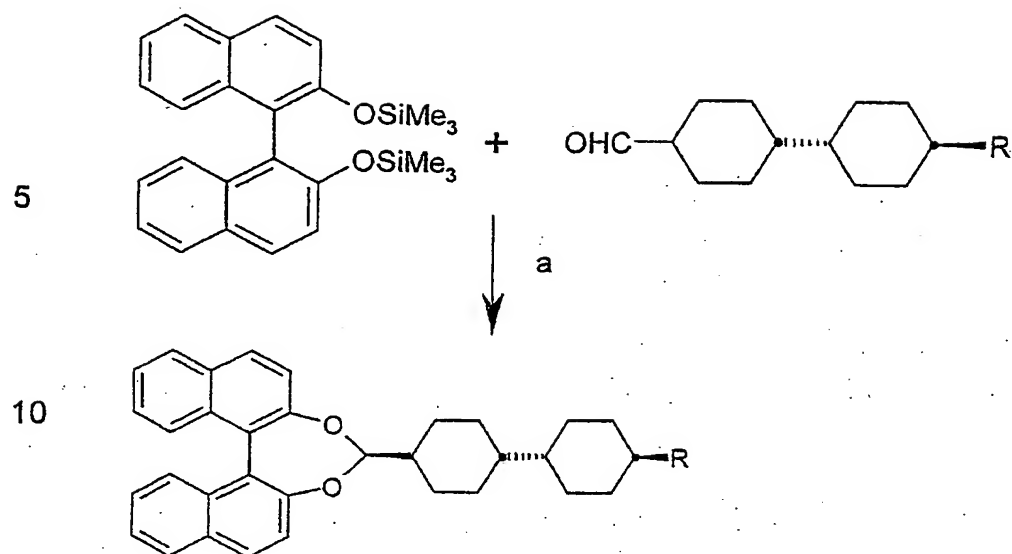


a) 1. CH_2Cl_2 , cat Me_3SiOTf , $-78^\circ\text{C} \rightarrow \text{RT}$; 2. pyridine

Scheme 2

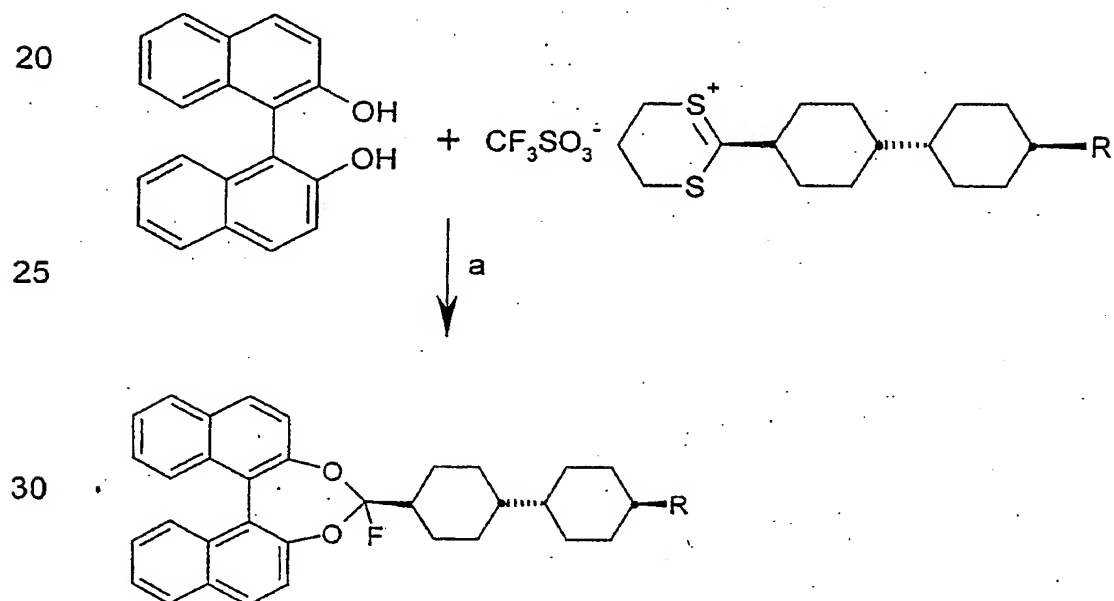
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35



15 a) 1. CH_2Cl_2 , cat Me_3SiOTf , $-78^\circ\text{C} \rightarrow \text{RT}$; 2. pyridine

Scheme 3



35 a) 1. NEt_3 , CH_2Cl_2 , -78°C ; 2. $\text{NEt}_3 \cdot 3\text{HF}$; 3. DBH; $-78^\circ\text{C} \rightarrow \text{RT}$
Me = methyl, Tf = triflate, R = C_{1-10} alkyl

5 The inventive chiral compounds can be used in a liquid crystal mixture for displays exhibiting a twisted molecular structure of the liquid crystal matrix like, for example, supertwisted or active matrix liquid crystal displays, or in displays comprising a liquid crystal mixture with a chiral liquid crystalline phase, like for example chiral smectic or chiral nematic (cholesteric) mixtures for ferroelectric displays or cholesteric displays.

10 Thus, another object of the invention is a liquid crystalline mixture, in particular a cholesteric liquid crystalline mixture, comprising at least one chiral compound of formula I.

15 Yet another object of the invention are cholesteric liquid crystal displays comprising a cholesteric liquid crystalline medium containing at least one chiral compound of formula I.

20 The inventive compounds are especially characterized by a high solubility in liquid crystalline host mixtures. Therefore, they can be added as dopants to liquid crystalline hosts in high amounts without significant affecting the phase behaviour and electrooptical properties of the mixture. Furthermore, undesired spontaneous crystallization at low temperatures are reduced and the operating temperature range of the mixture can be broadened.

25 Also, even inventive chiral compounds with low values of the HTP can be used for the preparation of highly twisted liquid crystal media, because the dopant concentration can be increased to yield low pitch values (i.e. high twist) without affecting the mixture properties. The use of a second dopant, which is often added to avoid crystallization, 30 can thus be avoided.

35 In addition, many of the inventive chiral compounds of formula I exhibit high values of the HTP. Thus liquid crystalline mixtures with a high helical twist, i.e. a low pitch, can be prepared by using the inventive compounds, or otherwise a liquid crystalline mixture with a

moderate helical twist can be achieved already when using the inventive compounds as dopants in low amounts.

5 The high HTP values of the inventive compounds makes them also suitable to be used in combination with other compounds for the temperature compensation of the properties of liquid crystal mixtures, such as the cholesteric pitch, and of the properties of displays, e.g. such as the threshold voltage.

10 As mentioned above, the inventive compounds are furthermore advantageous because they are affecting the physical properties of the liquid crystalline mixture only to a minor extent.

15 Thus, when admixing the chiral compounds of formula I for example to a liquid crystalline mixture with positive dielectric anisotropy that is used in a liquid crystal display, $\Delta\epsilon$ is being only slightly reduced and the viscosity of the liquid crystalline mixture is increased only to a small extent. This leads to lower voltages and improved switching times of the display when compared to a display comprising
20 conventional dopants.

A liquid crystalline mixture according to the invention comprises preferably 0.1 to 30 %, in particular 1 to 25 % and very particularly
25 preferably 2 to 15 % by weight of chiral compounds of formula I.

A liquid crystalline mixture according to the invention preferably comprises 1 to 3 chiral compounds of formula I.

30 For temperature compensation applications as described above the liquid crystalline mixture preferably contains a chiral component which contains at least one chiral compound of formula I, and a nematic component comprising one or more nematic or nematogenic compounds.

35 In a preferred embodiment of the invention the liquid crystalline mixture consist of 2 to 25, preferably 3 to 15 compounds, at least one

of which is a chiral compound of formula I. The other compounds, forming the nematic component, are preferably low molecular weight liquid crystalline compounds selected from nematic or nematogenic substances, for example from the known classes of the

5 azoxybenzenes, benzylidene-anilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl esters of cyclohexanecarboxylic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylcyclohexanecarboxylic acid, cyclohexylphenyl esters of

10 benzoic acid, of cyclohexanecarboxylic acid and of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclo-

15 hexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexylpyridazines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenyl-ethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)-ethanes, 1-cyclohexyl-2-biphenyl-ethanes, 1-phenyl-2-cyclohexyl-

20 phenylethanes, optionally halogenated stilbenes, benzyl phenyl ether, tolans, substituted cinnamic acids and further classes of nematic or nematogenic substances. The 1,4-phenylene groups in these compounds may also be laterally mono- or difluorinated.

25 The liquid crystalline mixture of this preferred embodiment is based on the achiral compounds of this type.

The most important compounds that are possible as components of these liquid crystalline mixtures can be characterized by the following

30 formula



35 wherein L' and E, which may be identical or different, are in each case, independently from one another, a bivalent radical from the group formed by -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-,

5 -Pyr-, -Dio-, -B-Phe- and -B-Cyc- and their mirror images, where Phe is unsubstituted or fluorine-substituted 1,4-phenylene, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and B is 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

10 G' in these compounds is selected from the following bivalent groups -CH=CH-, -N(O)N-, -CH=CY-, -CH=N(O)-, -C≡C-, -CH₂-CH₂-, -CO-O-, -CH₂-O-, -CO-S-, -CH₂-S-, -CH=N-, -COO-Phe-COO- or a single bond, with Y being halogen, preferably chlorine, or -CN.

15 R' and R'' are, in each case, independently of one another, alkyl, alkenyl, alkoxy, alkenyloxy, alkanoyloxy, alkoxy carbonyl or alkoxy carbonyloxy with 1 to 18, preferably 3 to 12 C atoms, or alternatively one of R' and R'' is F, CF₃, OCF₃, Cl, NCS or CN.

20 In most of these compounds R' and R'' are, in each case, independently of each another, alkyl, alkenyl or alkoxy with different chain length, wherein the sum of C atoms in nematic media generally is between 2 and 9, preferably between 2 and 7.

25 Many of these compounds or mixtures thereof are commercially available. All of these compounds are either known or can be prepared by methods which are known per se, as described in the literature (for example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for said reactions. Use may
30 also be made here of variants which are known per se, but are not mentioned here.

35 The inventive compounds are in particular useful for anisotropic polymer gels and for low molar mass or polymerizable or polymerized cholesteric liquid crystalline mixtures for cholesteric displays, such as

for example phase change displays or surface stabilized or polymer stabilized cholesteric texture displays (SSCT, PSCT).

5 A particularly preferred embodiment of the invention relates to chiral compounds showing a low temperature dependence of the HTP in nematic liquid crystal mixtures. These compounds are useful for cholesteric liquid crystalline mixtures and displays with a low temperature dependence of the reflection wavelength $d\lambda/dT$ (T = temperature, λ = reflection wavelength maximum).

10 In particular, it was found that when using chiral compounds of formula I in cholesteric liquid crystalline media, for example for application in an SSCT or PSCT display, they exhibit good solubility in the nematic host mixture and induce a high helical twist with low temperature dependence of the helical pitch and the reflection wavelength. Thus, cholesteric mixtures with high brightness of the reflection colour and low temperature dependence can be achieved even by using only one chiral dopant according to formula I, preferably in low amounts. This is a considerable advantage over prior art, where high amounts of dopants are needed, and where it is often necessary to use two or more dopants with opposite temperature dependence of the helical twist (e.g. one with positive temperature dependence and one with negative temperature dependence) to achieve good temperature compensation of the reflection wavelength.

25 Thus, a particularly preferred embodiment of the present invention relates to a cholesteric liquid crystalline medium, in particular for use in SSCT and PSCT displays, comprising one chiral compound of formula I, preferably in an amount of 15 % or less, in particular 10 % or less, very preferably 5 % or less.

30 Another preferred embodiment relates to inventive chiral compounds with a strong temperature dependence of the HTP in nematic liquid crystal mixtures, which are useful for thermochromic media.

35

Cholesteric displays are described for example in WO 92/19695, WO 93/23496, US 5,453,863 or US 5,493,430, with the entire disclosure of these documents being introduced into this application by way of reference.

5

Furthermore, anisotropic polymer gels and displays comprising them are disclosed for example in DE 195 04 224 and GB 2 279 659.

10

It has been found that SSCT and PSCT displays comprising the inventive compounds have reduced response times, lower voltages and improved contrast compared to displays comprising conventional dopants, like e.g. R 811 or CB 15, that are commercially available by Merck KGaA (Darmstadt, Germany). For example, SSCT and PSCT displays in which the conventional dopants are replaced by chiral compounds according to the present invention can show reduced switching time.

15

20

The chiral compounds according to the present invention are also suitable as chiral component in active broadband polymer stabilized liquid crystal displays as described for example in H. Guillard and P. Sixou, *Liq. Cryst.* (2001) **28(6)**, 933, the entire disclosure of which is incorporated into this application by reference. These displays comprise an active cholesteric layer with a broadened reflection wavelength band that is switchable between a planar reflective, a scattering and a homeotropic transparent state.

25

30

Cholesteric films made by using the inventive compounds instead of prior art dopants show improved brightness, leading to a better contrast between the coloured planar texture and the almost clear focal conic state which is made black using a black backplate.

35

The inventive chiral compounds and polymerizable liquid crystalline mixtures comprising these compounds are also particularly useful for the preparation of anisotropic polymer films with a chiral liquid crystalline phase, such as cholesteric or chiral smectic polymer films, in particular films that exhibit helically twisted molecular structure

with uniform planar orientation, i.e. wherein the helical axis is oriented perpendicular to the plane of the film.

5 For example, oriented cholesteric polymer films can be used as broad waveband reflective polarizers, as described e.g. in EP 0 606 940, as colour filters, for security markings, or for the preparation of liquid crystal pigments. I. Heynderickx and D.J. Broer in Mol.Cryst.Liq.Cryst. 203, 113-126 (1991) describe crosslinked cholesteric polymer films that are made of liquid crystalline
10 diacrylates and contain a low molecular weight chiral dopant.

It has been found that cholesteric polymer films made by using the inventive chiral compounds are brighter compared to films comprising dopants of prior art like e.g. R 811 or CB 15 as
15 mentioned above.

For the preparation of anisotropic polymer gels or oriented polymer films, the liquid crystalline mixture should comprise at least one polymerizable compound, preferably a polymerizable mesogenic compound, in addition to chiral compounds of formula I.
20

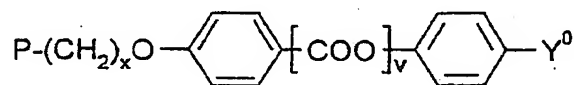
Thus, another object of the invention are polymerizable liquid crystalline mixtures comprising at least one chiral compound of formula I and at least one polymerizable mesogenic compound.
25

Examples of suitable polymerizable mesogenic compounds that can be used as components of the polymerizable CLC material, are disclosed for example in WO 93/22397; EP 0,261,712; DE 195,04,224; WO 95/22586 and WO 97/00600. The compounds
30 disclosed in these documents, however, are to be regarded merely as examples that shall not limit the scope of this invention.

Preferably the polymerizable CLC mixture comprises at least one polymerizable mesogenic compound having one polymerizable functional group and at least one polymerizable mesogenic compound having two or more polymerizable functional groups.
35

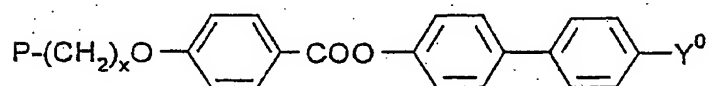
Examples of especially useful monoreactive chiral and achiral polymerizable mesogenic compounds are shown in the following list of compounds, which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention:

5



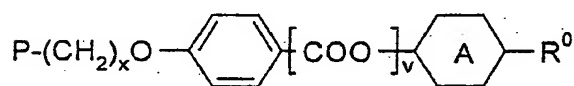
(Va)

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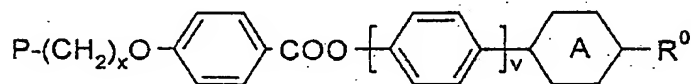


(Vb)

15

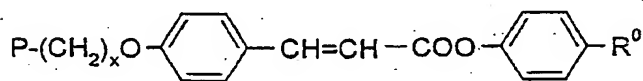


(Vc)



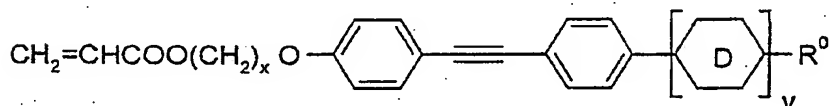
(Vd)

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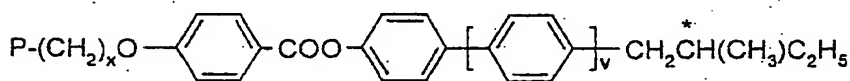
(Ve)

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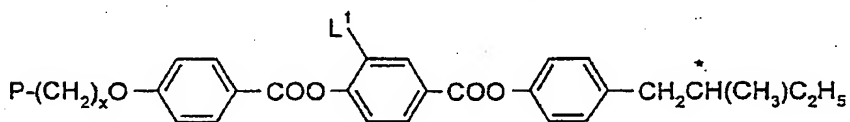


(Vf)

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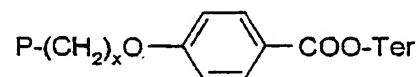


(Vg)

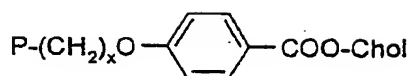


(Vh)

35

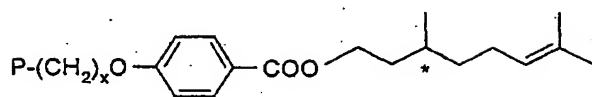


(Vi)



(Vk)

5



(Vm)

10

wherein, P has one of the meanings given above, x is an integer from 1 to 12, A and D are 1,4-phenylene or 1,4-cyclohexylene, v is 0 or 1, Y⁰ is a polar group, R⁰ is an unpolar alkyl or alkoxy group, Ter is a terpenoid radical like e.g. menthyl, Chol is a cholesteryl group, and L¹ and L² are each independently H, F, Cl, CN, OH, NO₂ or an optionally halogenated alkyl, alkoxy or carbonyl group with 1 to 7 C atoms.

15

The polar group Y⁰ is preferably CN, NO₂, halogen, OCH₃, OCN, SCN, COR⁵, COOR⁵ or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms. R⁵ is optionally fluorinated alkyl with 1 to 4, preferably 1 to 3 C atoms. Especially preferably the polar group Y⁰ is selected of F, Cl, CN, NO₂, OCH₃, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, C₂F₅, OCF₃, OCHF₂, and OC₂F₅, in particular F, Cl, CN, OCH₃ and OCF₃.

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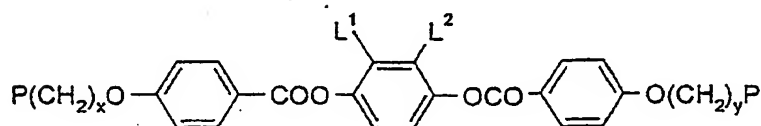
The unpolar group R⁰ is preferably an alkyl group with 1 or more, preferably 1 to 15 C atoms or an alkoxy group with 2 or more, preferably 2 to 15 C atoms.

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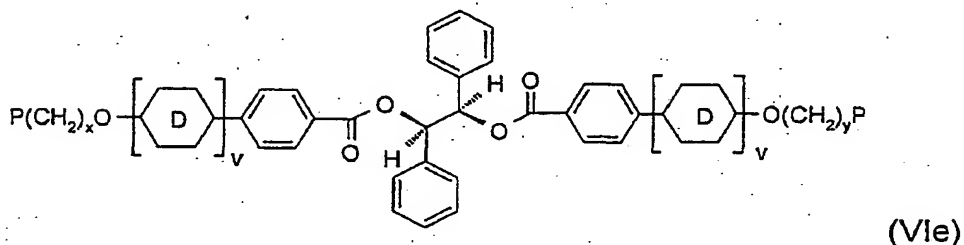
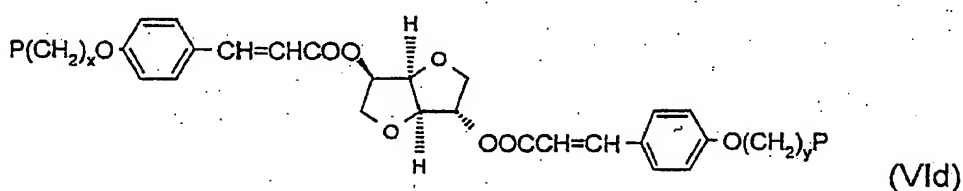
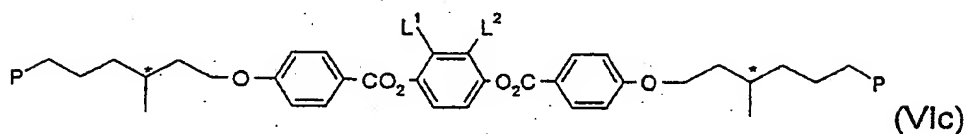
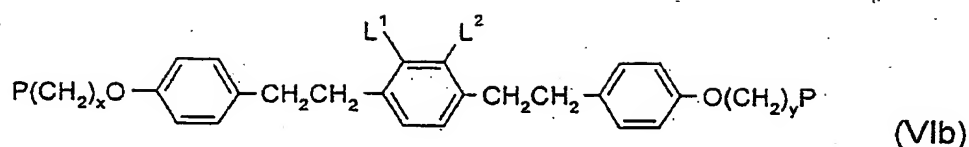
Examples of useful direactive chiral and achiral polymerizable mesogenic compounds are shown in the following list of compounds, which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention

30

35



(VIa)



wherein P, x, D, L¹ and L² have one of the meanings given above and y is an integer from 1 to 12 the same as or different from x.

25 A polymerizable CLC material according to the first preferred embodiment as described above comprises one or more chiral dopants which themselves do not necessarily have to show a liquid crystalline phase and give good planar alignment themselves, in particular non-polymerizable chiral dopants.

30 The mono- and difunctional polymerizable mesogenic compounds of above formulae V and VI can be prepared by methods which are known per se and which are described in the documents cited above and, for example, in standard works of organic chemistry such as, 35 for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

5 In a preferred embodiment of the invention the polymerizable liquid crystalline mixtures comprise at least one inventive chiral compound, at least one monofunctional compound of formulae Va-Vm and at least one bifunctional polymerizable compound of formulae VIa-VIe.

10 In another preferred embodiment the polymerizable liquid crystalline mixtures comprise at least one inventive chiral compound and at least two monofunctional compounds of formulae Va-Vm.

15 Another object of the invention is an anisotropic polymer film with an oriented chiral liquid crystalline phase obtainable by (co)polymerizing a liquid crystalline mixture comprising at least one chiral compound of formula I and at least one polymerizable mesogenic compound preferably selected of formula Va-Vm and VIa-VIe and/or at least one polymerizable chiral compound of formula I.

20 To prepare anisotropic polymer film with a chiral liquid crystalline phase with uniform orientation the inventive liquid crystalline mixtures, for example, are coated onto a substrate, aligned and polymerized in situ by exposing them to heat or actinic radiation. Alignment and curing are preferably carried out in the liquid crystalline phase of the liquid crystalline mixtures.

25 Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

30 For example, when polymerizing by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerization reaction.

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It is also possible to use a cationic photoinitiator, when curing reactive mesogens with for example vinyl and epoxide reactive groups, that photocures with cations instead of free radicals.

5 As a photoinitiator for radical polymerization for example the commercially available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerization the commercially available UVI 6974 (Union Carbide) can be used.

10 Preferably the polymerizable liquid crystalline mixtures comprising polymerizable chiral compounds of formula I and/or polymerizable mesogenic compounds of formulae V and VI additionally comprise 0.01 to 10 %, in particular 0.05 to 8 %, very preferably 0.1 to 5 % by weight of a photoinitiator, especially preferably a UV-photoinitiator.

15 In a preferred embodiment of the invention the polymerization of the polymerizable mesogenic material is carried out under an atmosphere of inert gas, preferably under a nitrogen atmosphere.

20 As a substrate for example a glass or quartz sheet as well as a plastic film or sheet can be used. It is also possible to put a second substrate on top of the coated mixture prior to, during and/or after polymerization. The substrates can be removed after polymerization or not. When using two substrates in case of curing by actinic radiation, at least one substrate has to be transmissive for the actinic radiation used for the polymerization.

25 Isotropic or birefringent substrates can be used. In case the substrate is not removed from the polymerized film after polymerization, preferably isotropic substrates are used.

30 Preferably at least one substrate is a plastic substrate such as for example a film of polyester such as polyethyleneterephthalate (PET), of polyvinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC), especially preferably a PET film or a TAC film. As a

35

birefringent substrate for example an uniaxially stretched plastic film can be used. For example PET films are commercially available from ICI Corp. under the trade name Melinex.

5 In a preferred embodiment of the present invention, the inventive mixture of the polymerizable liquid crystalline mixture comprising a chiral compound of formula I is coated as a thin layer on a substrate or between substrate, and is preferably aligned in its chiral mesophase, eg. the cholesteric or chiral smectic phase, to give a
10 planar orientation, i.e. an orientation so that the axis of the molecular helix extends transversely to the layer.

A planar orientation can be achieved for example by shearing the mixture, e.g. by means of a doctor blade. It is also possible to apply
15 an alignment layer, for example a layer of rubbed polyimide or sputtered SiO_x , on top of at least one of the substrates.

In another preferred embodiment, a second substrate is put on top of the coated material. In this case, the shearing caused by putting
20 together the two substrates is sufficient to give good alignment.

It is also possible to apply an electric or magnetic field to the coated mixture.

25 In some cases it is of advantage to apply a second substrate not only to aid alignment of the polymerizable mixture but also to exclude oxygen that may inhibit the polymerization. Alternatively the curing can be carried out under an atmosphere of inert gas. However, curing in air is also possible using suitable photoinitiators and high
30 lamp power. When using a cationic photoinitiator oxygen exclusion most often is not needed, but water should be excluded.

A detailed description of the in situ polymerization of polymerizable mesogenic compounds can be found in D.J.Broer et al.,
35 Makromolekulare Chemie 190, 2255 (1989).

A polymerizable liquid crystalline mixture for the preparation of anisotropic polymer films comprises preferably 0.1 to 35 %, in particular 0.5 to 15 % and very particularly preferably 0.5 to 5 % by weight of one or more polymerizable chiral compounds of formula I.

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Polymerizable liquid crystalline mixtures are preferred that comprise 1 to 3 chiral compounds of formula I.

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The inventive polymerizable liquid crystalline mixtures can additionally comprise one or more other suitable components, such as, for example, catalysts, sensitizers, stabilizers, co-reacting monomers or surface-active compounds.

15

In a preferred embodiment of the invention, the inventive polymerizable liquid crystalline mixture comprises a stabilizer that is used to prevent undesired spontaneous polymerization for example during storage of the composition. As stabilizers in principal all compounds can be used that are known to the skilled in the art for this purpose. These compounds are commercially available in a broad variety. Typical examples for stabilizers are 4-ethoxyphenol or butylated hydroxytoluene (BHT).

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It is also possible, in order to increase crosslinking of the polymers, to add up to 20% of a non mesogenic compound with two or more polymerizable functional groups to the polymerizable composition alternatively or additionally to the multifunctional polymerizable mesogenic compounds.

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Typical examples for difunctional non mesogenic monomers are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples for non mesogenic monomers with more than two polymerizable groups are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

35

Polymerization of inventive compositions comprising compounds with only one polymerizable functional group leads to linear

polymers, whereas in the presence of compounds with more than one polymerizable functional group crosslinked polymers are obtained.

- 5 For the preparation of anisotropic polymer gels, the liquid crystalline mixtures can be polymerized in situ as described above, however, in this case alignment of the polymerizable mixture is not necessary.

- 10 The inventive chiral compounds of formula I can also be used for the preparation of thermochromic liquid crystalline mixtures. Such mixtures are characterized in that they exhibit a chiral liquid crystalline phase or chiral mesophase, like e.g. a chiral smectic phase or a chiral nematic (= cholesteric) phase, with a helically twisted molecular structure that shows selective reflection of a
15 specific waveband of light, wherein the pitch of the molecular helix and thereby the reflected wavelengths are depending on the temperature.

- 20 Especially preferred are inventive liquid crystalline mixtures with thermochromic behaviour that exhibit a cholesteric phase. Of these preferred compositions, further preferred are compositions that exhibit a cholesteric phase and a smectic phase, most preferably a chiral smectic phase, at temperatures below the temperature range of the cholesteric phase. The inventive liquid crystalline mixtures
25 exhibiting thermochromic behaviour can be polymerizable or non-polymerizable.

- 30 The inventive chiral compounds of formula I and liquid crystalline mixtures, liquid crystal polymers or liquid crystal pigments comprising them are also suitable for use in cosmetic and pharmaceutical compositions, for example for coloured make-up as described in EP 815 826 or as UV-filters for the protection of human skin or hair, in particular protection against UV-A and UV-B-radiation, as described
35 for example in DE 196 29 761 or EP 1 038 941. The inventive dopants have a high HTP, therefore only small amounts are needed.

to yield a short pitch, resulting in a material that shows reflection in the UV range and is suitable as UV-filter.

5 A liquid crystalline mixture, liquid crystal polymer or liquid crystal pigment comprising a chiral compound of formula I and reflecting UV light, in particular of a wavelength of 200 to 400 nm, is another object of the invention. Another object is a cosmetic composition, in particular a cosmetic or pharmaceutical composition for protection of human skin or hair, comprising as UV-filter a liquid crystalline
10 mixture, liquid crystal polymer or liquid crystal pigment comprising a chiral compound of formula I and reflecting UV light, in particular in a wavelength range of 200-440 nm, especially 280-400 nm, 200-230 nm (UV-C) and 280-330 nm (UV-B).

15 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

20 Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.
25

In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight.

30 The values of the helical twisting power HTP of a chiral compound in a liquid crystalline host are given according to the equation $HTP = (p \cdot c)^{-1}$ in μm^{-1} , wherein p is the pitch of the molecular helix, given in μm , and c is the concentration by weight of the chiral compound in the host given in relative values (thus, e.g. a concentration of 1 % by weight is corresponding to a value of c of 0.01).
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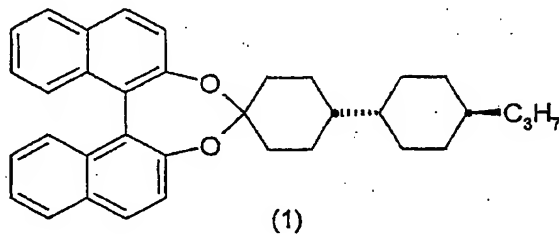
The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds: C = crystalline; N = nematic; S = smectic; N*, Ch = chiral nematic or cholesteric; I = isotropic. The numbers between these symbols indicate the phase transition temperatures in degree Celsius. Furthermore, mp. is the melting point, Δn is the birefringence at 589 nm and 20 °C and $\Delta \epsilon$ is the dielectric anisotropy at 20 °C. λ is the reflection wavelength [nm] at a given temperature, or at a temperature of 20 °C unless stated otherwise. $\Delta \lambda$ is the maximum variation of the reflection wavelength [nm] within a given temperature range, or between - 20 °C and + 70 °C unless stated otherwise.

C* in a chemical formula denotes a chiral C atom. DCM is dichloromethane. "Conventional workup" means: water is added if necessary, the mixture is extracted with methylene chloride, diethyl ether or toluene, the phases are separated, the organic phase is dried and concentrated by evaporation, and the product is purified by crystallization and/or chromatography.

Unless indicated otherwise, the HTP values of the examples were determined in the commercially available liquid crystal host mixture MLC-6260 (Merck KGaA, Darmstadt, Germany) at a concentration of 1 % and a temperature of 20 °C.

Example 1

Compound (1) was prepared according to above reaction scheme 1.



a) Preparation of 2,2'-Bis-trimethylsilyloxy-[1,1']binaphthalenyl

According to methods known from the literature, bisphenol is reacted with 2.2 eq. of Me_3SiCl in NEt_3/DMF 1:1 and worked up in the conventional way, with recrystallization from n-heptane.

b) Preparation of (1)

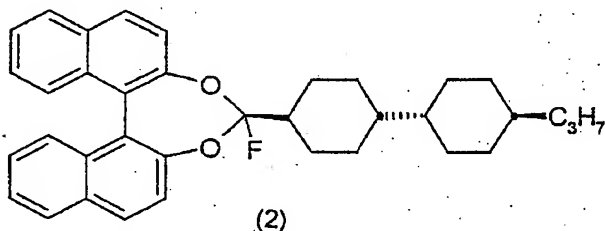
b) A solution of 10.007 g (0.045 mol) 4'-propyl-bicyclohexyl-4-one in 50 ml DCM is added to 21.535 g (0.050 mol) 2,2'-bis-trimethylsilanyloxy-[1,1']binaphthalenyl in 50 ml DCM. After stirring at room temperature a small amount of pyridine is added dropwise and the reaction mixture poured into 200 ml sat. aq. solution of NaHCO_3 . The separated aqueous phase is extracted with DCM and the combined organic phases dried over Na_2SO_4 . The crude product is recrystallized from toluene to give colourless crystals.

Properties: mp. 220 °C

HTP 22.7 (0°C), 24.7 (20°C), 26.0 (50°C)

Example 2

Compound (2) was prepared according to above reaction scheme 3.



a) Preparation of triflate

60.73 ml (0.69 mol) trifluoromethylsulfonic acid are added dropwise to 57.96 g (0.23 mol) 4'-propyl-bicyclohexyl-4-carboxylic acid and 25.00 g (0.23 mol) propanedithiol and the mixture heated to 120 °C for 45 minutes. After cooling 800 ml diethyl ether are added and the

solution cooled to 0 °C for 5 hours. The precipitated product is filtered off, washed with diethyl ether and dried in vacuum.

b) Preparation of (2)

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At -65 °C a solution of 10.00 g (0.035 mol) [1,1']binaphthalenyl-2,2'-diol and 5.325 ml (0.038 mol) triethylamine in 50 ml DCM is added dropwise to 36.47 g (0.077 mol) of the triflate from a) in 300 ml DCM. After stirring for 90 minutes and addition of 63.9 ml (0.384 mol) triethylamine-trishydrofluoride a suspension of 109.8 g (0.384 mol) 1,3-Dibromo-5,5-dimethylhydantoin (DBH) in 150 ml DCM is added in small portions. The orange suspension is heated to -20 °C and poured onto a mixture of 1500 ml 1M NaOH solution and 150 ml NaHSO₃ solution. The separated aqueous phase is extracted with DCM and the combined organic phases dried over Na₂SO₄. After evaporation of the solvent the residue is filtered in petroleum ether / ethyl acetate-50:1 with silica gel. The colourless crude product is suspended in 100 ml abs. ethanol, 10 ml of aq. KOH solution are added and the mixture stirred for 1 hour at room temperature. 1000 ml MTB ether are added, the solution washed with 1M NaOH and water and dried over Na₂SO₄. After evaporation of the solvent a green solid is obtained. The crude product is separated by preparative HPLC and purified by recrystallization from toluene / pentane.

Properties: mp. 230 °C

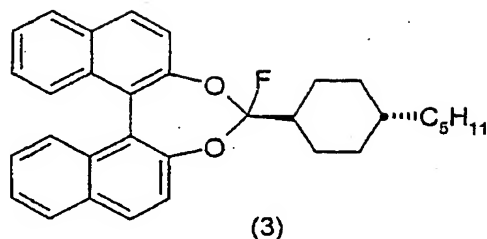
HTP -67 (0°C), -71 (20°C), -72 (50°C)

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The following compounds were prepared analogously:

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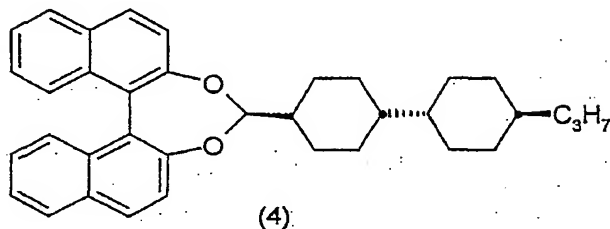
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mp. 143 °C

HTP 62 (0°C),
65 (20°C), 65 (50°C)

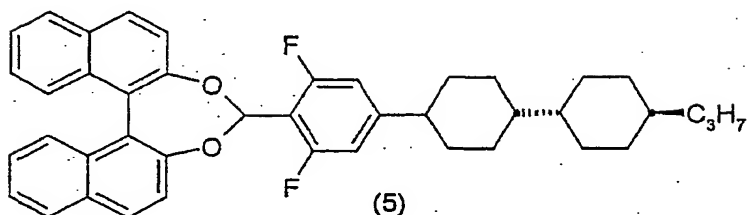
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mp. 205 °C

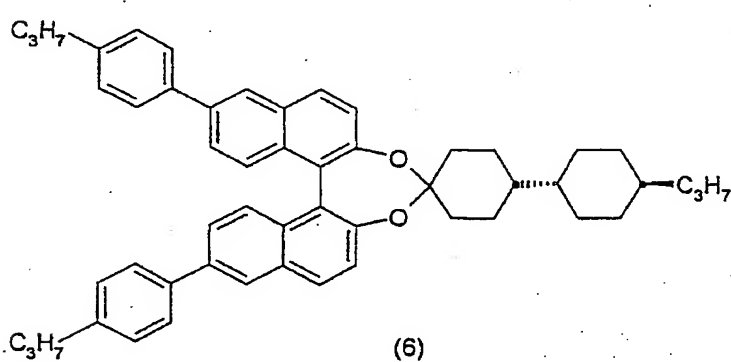
HTP 82 (0°C),
86 (20°C), 90 (50°C)

15



HTP 46 (20°C),

20



HTP 29 (20°C)

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Use Example A

Cholesteric liquid crystal mixtures are formulated comprising the following nematic liquid crystal host mixture

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K6	8.0 %	Kp.	98.4
K9	9.0 %	Δn	0.1786

5	ME3N.F	10.0 %	n_e	1.6836
	ME4N.F	10.0 %	$\Delta\epsilon$	+31.1
	BCH-5	10.0 %	$\epsilon_{ }$	38.3
	HP-3N.F	7.0 %	γ_1	373
	HP-4N.F	5.0 %		
10	HP-5N.F	5.0 %		
	CBC-33	2.0 %		
	CBC-33F	3.0 %		
	CBC-53	3.0 %		
	CBC-55F	3.0 %		
	CC-5-V	13.0 %		
	ME2N.F	8.0 %		
	ME5N.F	4.0 %		

15 and further comprising small amounts of chiral dopants according to example 2. The properties of the cholesteric mixtures are shown in table 1.

Table 1

20	Mix. No.	Dopant	Dopant Concentration	λ [nm]	$\Delta\lambda$ [nm]
	A1	(2)	3.4 %	506	13
	A2	(3)	4.0 %	479	29
	A3	(4)	2.8 %	536	25

25

The mixtures exhibit low temperature dependence of the reflection wavelength.

30

The mixtures exhibit low temperature dependence of the reflection wavelength.

Use Example B

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Cholesteric liquid crystal mixtures are formulated comprising the following nematic liquid crystal host mixture

5	PCH-2	6.0 %	Kp.	87.5
	PCH-3	18.0 %	Δn	0.2417
	ME2N.F	2.0 %	n_e	1.7552
	ME3N.F	3.0 %	$\Delta \varepsilon$	+18.8
	ME4N.F	8.0 %	$\varepsilon_{ }$	24.3
10	ME5N.F	8.0 %	γ_1	211
	PCH-302	4.0 %		
	PPTUI-3-2	20.0 %		
	PPTUI-3-4	31.0 %		

and further comprising small amounts of chiral dopants according to example 2. The properties of the cholesteric mixtures are shown in table 2.

Table 2

15	Mix. No.	Dopant	Dopant Concentration	λ [nm]	$\Delta \lambda$ [nm]
	B1	(2)	3.8 %	520	38
20	B2	(3)	4.0 %	544	22
	B3	(4)	3.0 %	557	47

The mixtures exhibit low temperature dependence of the reflection wavelength.

25 Use Example C

Cholesteric liquid crystal mixtures are formulated comprising the following nematic liquid crystal host mixture

30	PCH-2	6.0 %	Kp.	87.5
	PCH-3	18.0 %	Δn	0.2417
	ME2N.F	2.0 %	n_e	1.7552
	ME3N.F	3.0 %	$\Delta \varepsilon$	+18.8
	ME4N.F	8.0 %	$\varepsilon_{ }$	24.3
35	ME5N.F	8.0 %	γ_1	211
	PCH-302	4.0 %		

PPTUI-3-2 20.0 %
PPTUI-3-4 31.0 %

and further comprising small amounts of chiral dopants according to
example 2. The properties of the cholesteric mixtures are shown in table 3.

Table 3

Mix. No.	Dopant	Dopant Concentration	λ [nm]	$\Delta\lambda$ [nm]
C1	(3)	4.1 %	527	29
C2	(4)	3.1 %	547	78

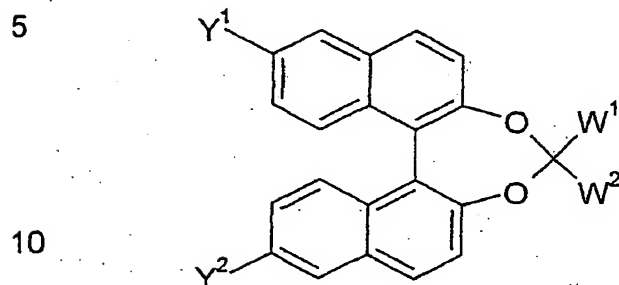
The mixtures exhibit low temperature dependence of the reflection
wavelength.

The preceding examples can be repeated with similar success by
substituting the generically or specifically described reactants and/or
operating conditions of this invention for those used in the preceding
examples.

From the foregoing description, one skilled in the art can easily
ascertain the essential characteristics of this invention, and without
departing from the spirit and scope thereof, can make various
changes and modifications of the invention to adapt it to various
conditions and usages.

Patent Claims

1. Chiral binaphthol derivatives of formula I



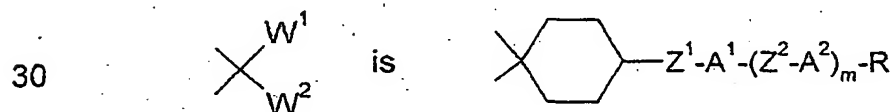
wherein

15 Y¹ and Y² are independently of each other H, F, Cl, Br, I, CN, SCN, SF₅, or a chiral or achiral alkyl group with up to 30 C atoms which may be unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or a polymerizable group,

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one of W¹ and W² is -Z¹-A¹-(Z²-A²)_m-R and the other is H, R² or A³, or



35 Z¹ and Z² are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-N(R¹)-, -N(R¹)-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-,

-CF₂CF₂-, -CH=CH-, -CF=CH-, -CH=CF-, -CF=CF-,
-C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

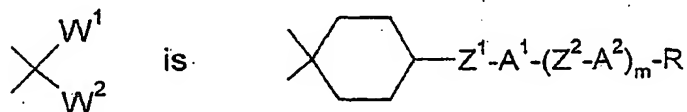
R¹ is H or alkyl with 1 to 4 C atoms,

A¹, A² and A³ are independently from one another 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, 1,3-dioxolane-4,5-diyl, 1,4-cyclohexenylenes, 1,4-bicyclo-(2,2,2)-octylene, piperidine-1,4-diyl, naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl or indane-2,5-diyl, it being possible for all these groups to be unsubstituted, mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl groups with 1 to 7 C atoms, wherein one or more H atoms may be substituted by F or Cl, and A¹ may also be a single bond,

m is in each case independently 0, 1, 2 or 3, and

R and R² have independently of each other one of the meanings given for Y¹.

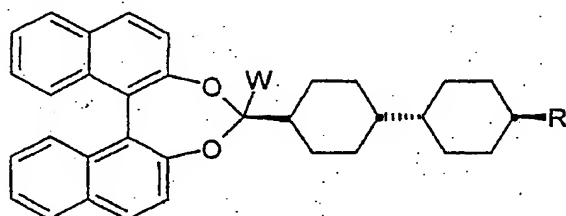
2. Chiral binaphthol derivatives according to claim 1, wherein W¹ is H and W² is -Z¹-A¹-(Z²-A²)_m-R with m being 1 or 2.
3. Chiral binaphthol derivatives according to claim 1, wherein



and m is 0 or 1.

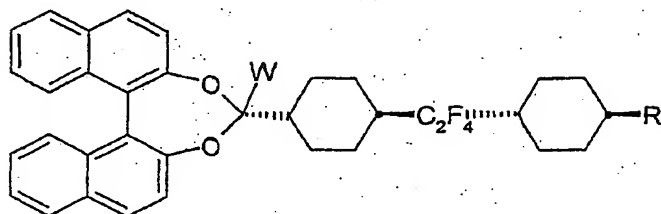
4. Chiral binaphthol derivatives according to at least one of claims 1 to 3, selected of the following formulae

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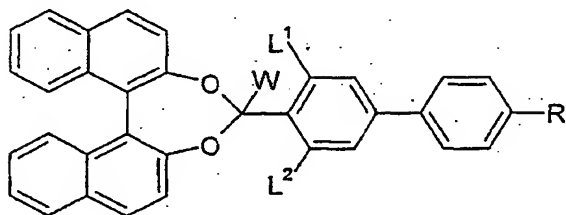
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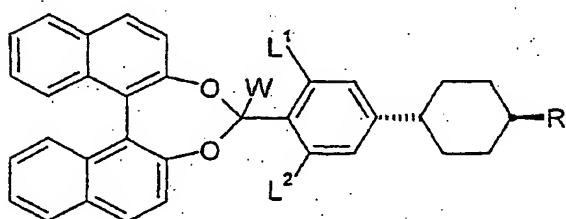
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1c

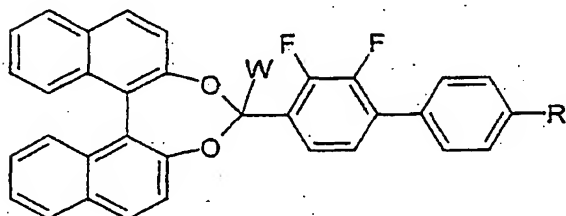
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1d

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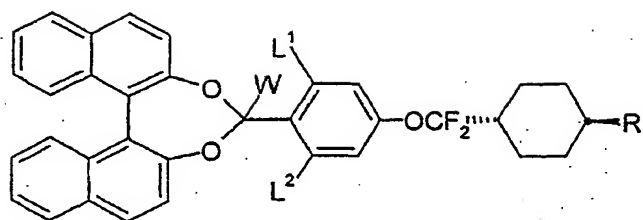
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1e

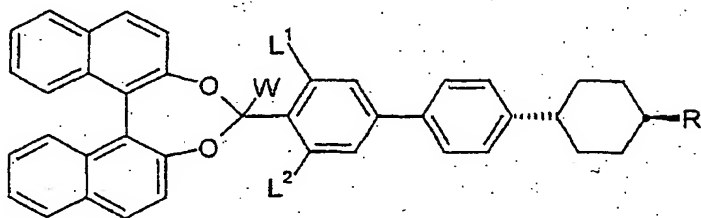
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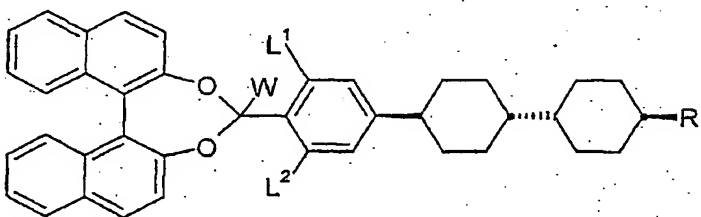
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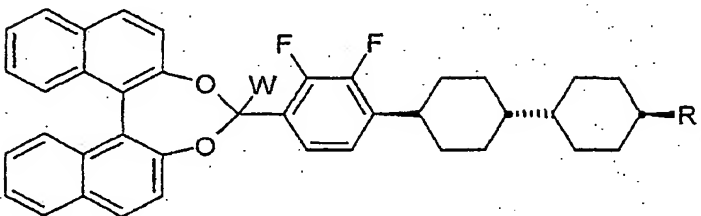
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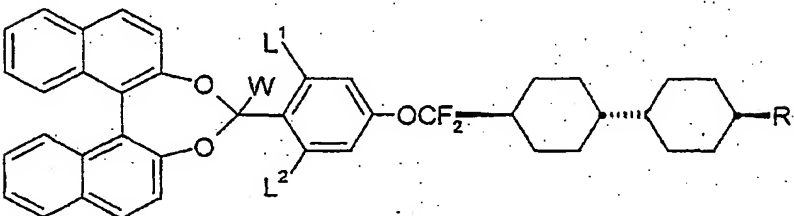
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Ii

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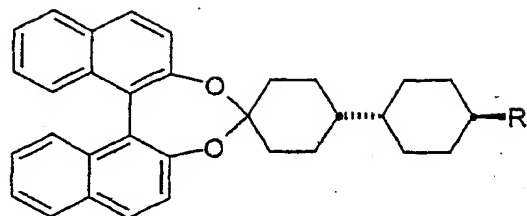


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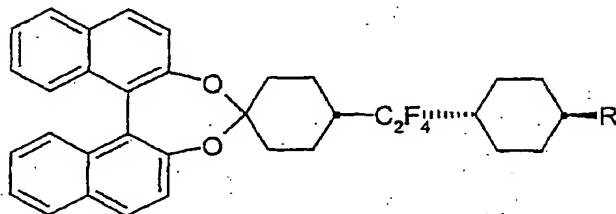
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Im

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wherein R has the meaning of claim 1, L^1 and L^2 are H or F and W is H, F, alkyl or alkoxy with 1 to 12 C atoms, cyclohexyl or phenyl that can be substituted in 1 to 4 positions with F, Cl, CN or an optionally fluorinated alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl group having 1 to 4 C atoms.

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5. Chiral binaphthol derivatives according to at least one of claims 1 to 4, wherein one of Y^1 , Y^2 and R is a polymerizable group P-Sp-X, with

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P being $CH_2=CW-COO-$, $WCH=CH-O-$, $WHC-\text{CH}_2-\text{CH}-$ or $CH_2=CH-Phenyl-(O)_k-$, W being H, CH_3 or Cl and k being 0 or 1,

30

Sp being a spacer group having 1 to 25 C atoms or a single bond,

X being -O-, -S-, -OCH₂-, -CH₂O-, -CO-, -COO-, -OCO-, -OCO-O-, -CO-N(R¹)-, -N(R¹)-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CH=CH-COO-, -OOC-CH=CH- or a single bond, and

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R¹ being H or alkyl with 1 to 4 C atoms.

6. A liquid crystalline mixture comprising at least one chiral binaphthol derivative according to at least one of claims 1 to 5.
- 5 7. A liquid crystalline mixture according to claim 6, further comprising at least one polymerizable mesogenic compound having at least one polymerizable functional group.
8. A chiral linear or crosslinked liquid crystalline polymer obtainable by polymerizing a mixture according to claim 6 or 7.
- 10 9. Use of a chiral binaphthol derivative, mixture or polymer according to at least one of claims 1 to 8 in liquid crystal displays, like for example STN, TN, AMD-TN, temperature compensation, ferroelectric, guest-host, phase change or surface stabilized or
15 polymer stabilized cholesteric texture (SSCT, PSCT) or active broadband polymer stabilized liquid crystal displays, in active and passive optical elements like polarizers, compensators, alignment layers, colour filters or holographic elements, in adhesives, synthetic resins with anisotropic mechanical properties, cosmetic
20 or pharmaceutical compositions for example as UV filters, diagnostics, liquid crystal pigments, for decorative and security applications, in nonlinear optics, optical information storage or as chiral dopants.
- 25 10. A liquid crystal display comprising a liquid crystalline mixture according to claim 6 or 7.
11. A cholesteric liquid crystalline medium comprising a chiral component which contains one or more chiral binaphthol
30 derivatives according to at least one of claims 1 to 6, and a nematic component which contains one or more nematic or nematogenic compounds.
12. An SSCT, PSCT or active broadband polymer stabilized liquid
35 crystal display comprising a medium according to claim 12.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 01/11075

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D321/10 C09K19/34 C09K19/58 //C07M7:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KUBALL H-G ET AL: "CHIRALITY AND CIRCULAR DICHROISM OF ORIENTED MOLECULES AND ANISOTROPIC PHASES" CHIRALITY, WILEY-LISS, NEW YORK, US, vol. 12, no. 4, 2000, pages 278-286, XP001041318 ISSN: 0899-0042 the whole document — -/-	1-12

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Further documents are listed in the continuation of box C.

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Patent family members are listed in annex.

* Special categories of cited documents:

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- *E* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

7 February 2002

Date of mailing of the international search report

27/02/2002

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INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/EP 01/11075

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>ZHANG M. ET AL.: "Chirochromism-photo-chromism by epimerization: search for a liquid crystal phototrigger" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 116, no. 11, - 1 June 1994 (1994-06-01) pages 4852-4857, XP002189468 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC., US ISSN: 0002-7863 the whole document</p>	1-12